



Photocatalytic Degradation of Azo Dyes by Pure and Aluminium Doped CdO Nanocrystalline Thin Films

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ABSTRACT

Pure and Al-doped Cadmium oxide (CdO) nanocrystalline thin films were synthesized by using the chemical bath deposition method and annealed at 500°C. The films were characterized to study their structural, optical and compositional properties. The films were used to degrade the azo dyes, methylene blue (MB) and methyl orange (MO) using photocatalytic activity (PCA). It was found that the films were capable of degrading MB up to 19% and were able to decolorize MO them up to 30%

Keywords: Al doped CdO; Azo dyes; Cadmium oxide; Photo-catalytic activity.

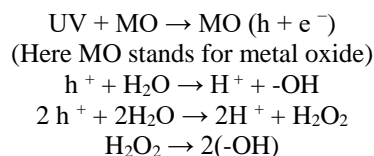
1. INTRODUCTION

Organic chemicals found as pollutants in wastewater effluents from industrialized sources must be destroyed before discharging to the environment. Such pollutants may also be found in ground and surface waters which also need treatment to achieve acceptable drinking water quality. Among various methods, photocatalysis has gained a lot of notice in the field of pollutant degradation.

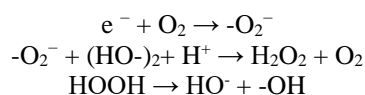
One of the major advantages of the photocatalytic process is that there is no additional requirement for secondary disposal methods. Another benefit is that when compared to other advanced oxidation technologies, especially those using oxidants such as hydrogen peroxide and ozone, expensive oxidizing chemicals are not required as ambient oxygen is the oxidant (Mathews, 1993; Rajachandrasekar *et al.* 2016). Photocatalysts are also self-regenerated and can be reused or recycled.

Photo-catalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photo generated catalysis, the photocatalytic activity (PCA) depends on the capability of the catalyst to generate electron-hole pairs, which create free radicals (e.g. hydroxyl radicals: -OH) that are capable of experiencing secondary reactions. A reaction between the excited electrons with an oxidant to produce a reduced product to produce an oxidized product takes place. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place on the surface of semiconductors. In the oxidative reaction, the

positive holes respond with the moisture present on the surface and generate a hydroxyl radical. Oxidative reactions due to photocatalytic effect are as follows:



The reductive reaction due to photocatalytic effect:



Requirements for an efficient photocatalytic material include (i) an ability to generate electron-hole pairs and prevent re-combination long enough for the electrons and holes to reach the surface of the thin film, (ii) activation by sunlight (iii) inexpensive and easy to produce (iv) chemically inert (v) physically adherent and strong.

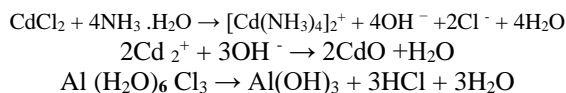
Henamsylvia Devi and Thiyam David Singh prepared Copper nanoparticles using *Centella asiatica* L. leaves extract at room temperature for the photocatalytic degradation of methyl orange. These nanoparticles reduced methyl orange to its leuco form in aqueous medium in the absence of reducing agents. This catalytic effect of copper oxide nanoparticles contributed to its small size. Copper oxide nanoparticles such as prepared had good catalytic properties. Beydoun *et al.* 1998 gave an overview of the development and implications of nanotechnology in photocatalysis. The use of

nanocrystalline thin films in electrochemically assisted photocatalytic processes.

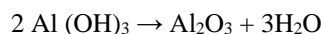
2. EXPERIMENTAL METHODS

2.1 Synthesis of pure and Al doped CdO thin films

In the present work, Cadmium Oxide (CdO) thin films were prepared on glass substrates by sol-gel chemical bath deposition technique. In a conical flask, 0.1M of Cadmium chloride ($\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$) was dissolved in 250ml of deionized water. The solution was continuously stirred by a magnetic stirrer for 1 hour to get a clear homogeneous solution. Ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) solution was added with this solution drop-wise till the pH is reached 12. The solution is taken in small beakers, and the glass substrates were immersed to about 5 cm into beakers for 24 hours. The glass slides were dried in a hot air oven. These slides were annealed to 500 °C. The undoped CdO thin film was prepared. The same procedure was continued to dope aluminum to CdO. Anhydrous aluminum chloride (AlCl_3) was added to the pure CdO precursor in the beaker (Anour Hajjaji, 2014; Ramiz Ahmed Al-Ansari, 2016). The results obtained for the lesser concentrations of 1% and 2% of Al doping exhibit similar results for XRD analysis. So 3wt% Al doping was optimized. This solution is stirred using a magnetic stirrer for 2 hours. The glass substrates were dipped into the beaker for 24 hours.



Aluminum Oxide is formed from the Aluminum Hydroxide on strong heating (~400°C) via:



The glass substrates were dried using a hot air oven and annealed at 500 °C.

Al was chosen as a dopant to organize and improve the properties of CdO thin films. Al^{3+} ion has three valence electrons, and the ionic radius of Al^{3+} ion (0.68 Å) is slightly smaller than that of Cd^{2+} ions (0.95 Å). Thus Al^{3+} ions doping in CdO will direct to enhancement in electrical conductivity by increasing electron concentration (Saleh and Gupta, 2012). Since Al^{3+} has a lesser ionic radius than that of Cd, there would be a significant difference in its electrical property (Azadeh *et al.* 2014). This is attainable by a shift in the optical band gap along with the enhancement in the transparency of CdO films (Beydoun *et al.* 1998).

2.2 Photo-catalytic Activity Test

The photocatalytic activity of CdO nanoparticles can be studied using methylene blue

[$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$] and methyl orange [$\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$], the widely used azo dyes. The CdO thin films synthesized were dipped in methylene blue and methyl orange solutions. The methylene blue was examined by using a UV-Visible Spectrophotometer. The maximum absorption was found to be at a wavelength of 675nm. The maximum absorbance of MB is around 661nm-665nm (Cheng *et al.* 2013; Azzaryiatul Hafizah Amar, 2007). Methyl orange solution was treated with UV-Visible light, which gave a maximum absorption at a wavelength of 465nm. The maximum absorbance of methyl orange is approximately 462 nm in the visible region. The concentration of both dyes was prepared to be 10 ppm. Irradiation of the solutions was carried out under UV-Vis light (6 lamps with a power of 20 W, Philips).

The experiment was executed as follows: The maximum absorbance of both methylene blue solution and methyl orange solution was measured, and then to that wavelength, absorbance was noted for the degradation of the dye before and after the addition of metal oxide. This absorbance is noted to be A_0 . After UV irradiation, the absorbance was again measured at 't' intervals of time. For every hour, the absorbance value is noted. The total irradiation time is 5 hours. The extent of the photocatalytic activity of CdO in methylene blue and methyl orange can be determined by measuring the absorbance of the solutions. The degradation of the dyes can be evaluated by using the formula:

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

Where A_0 represents the initial absorbance and A_t signifies the absorbance after t min reaction of the dyes at the characteristic absorption wavelength of 675 nm.

According to the principles of CdO photo catalyst, the energy gap is created on the surface of Cadmium oxide when are given radiation in photon light with either greater than or equal the bandgap energy, and an electron may be advanced from the valence band to the conduction band ($e^- c_b$) leaving behind an electronic vacancy or "hole" in the valence band ($h^+ v_b$). If charge separation is sustained, the electron and hole may transfer to the catalyst surface, where they take part in redox reactions with the sorbed species.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Analysis

The structural properties of CdO nanoparticles were investigated using an X-ray diffraction analysis. The existence of multiple diffraction peaks of (011), (111), (200), (220), (311), and (222) planes specifies the polycrystalline nature of the CdO with cubic structure (Comparelli *et al.* 2005; Ngamnit Wongcharoen *et al.*

2012). The XRD pattern exposed diffraction peaks approximately at 33° , 38° , 55.5° and 68° of 2θ values, indicating the hkl values as (1 1 1), (2 0 0), (2 2 0), and (2 2 2) which corresponds to polycrystalline having the characteristic peaks of face-centered cubic structure of CdO (JCPDS Card No. 05-0640, 73-2245 and 78-065) (Fateneg *et al.* 2013; Hamadani *et al.* 2013; Harraz *et al.* 2014; Hussein, 2013; Gbadebo Taofeek Yusuf *et al.* 2016; Kumaravel *et al.* 2010; Ngamnit Wongcharoen *et al.* 2012; Saha *et al.* 2007) and it is shown in Fig. 1(a).

The sharp peak values are used to calculate the lattice parameter and grain size. Doping CdO films with Al causes a small reduction in the intensity of all peaks and especially of the (2 0 0) plane, and it is shown in Fig. 1(b). The Al-doped CdO films have (1 1 1) plane as the preferred orientation, and it is similar to the results reported by Saha *et al.* 2007 (Hussein, 2013). The crystalline nature and the intensity of the peak of (1 1 1) in the diffraction pattern are increased with an increase in Al doping concentration, showing that the doping helps in the nucleation and growth of grains. The crystallite size (D) was calculated from the full width at half maximum (FWHM) β of the major XRD peaks using Scherrer-Bragg's relation (Jiang *et al.* 2013) (Behnaz Afzalian Mend *et al.* 2017).

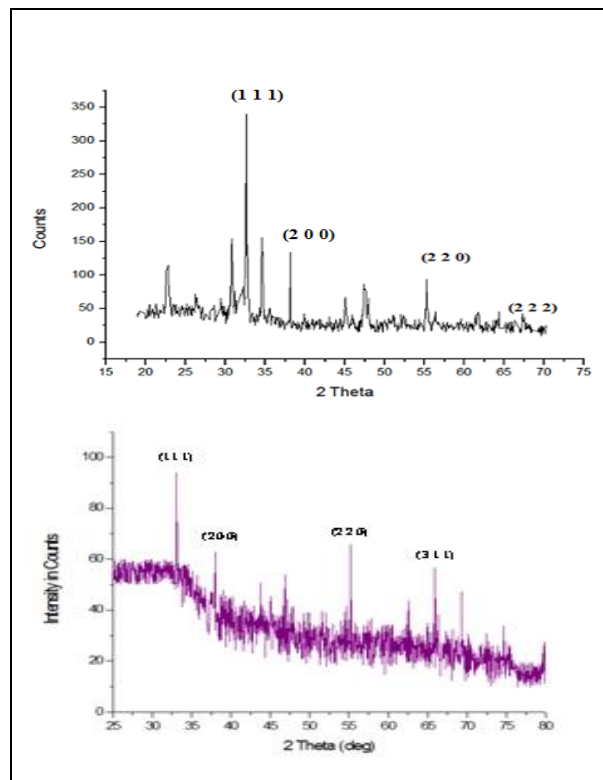


Fig. 1: XRD spectrum of (a) pure and (b) Al doped CdO thin films

Table 1. Structural values of CdO films

| Film | 2θ (deg) | FWHM (radians) | Lattice strain | Dislocation density $\times 10^{14}$ (δ) lines/m ² | Micro strain(ϵ) (10^4 lin ⁻² m ⁻⁴) | Average crystallite size (D) in nm |
|----------------|--------------------|-------------------|-------------------|--|--|--|
| Pure CdO | 15.2526 | 0.3444 | 0.0225 | 17.1319 | 9.0365 | 38.76 |
| | 18.3321 | 0.1476 | 0.0080 | 03.1414 | 8.7565 | |
| | 22.6727 | 0.1968 | 0.0087 | 05.5651 | 6.8558 | |
| | 26.3868 | 0.5904 | 0.0223 | 49.9450 | 4.2314 | |
| | 29.0478 | 0.1476 | 0.0051 | 03.1105 | 5.5734 | |
| Al:CdO 3wt% | 5.7385 | 0.5063 | 0.0882 | 37.18024 | 20.67552 | 28.148 |
| | 18.2243 | 0.5196 | 0.0285 | 38.91642 | 6.48847 | |
| | 31.8419 | 0.1299 | 0.0041 | 2.401467 | 5.160884 | |
| | 66.5304 | 0.9092 | 0.0133 | 110.1068 | 1.422715 | |
| | 84.4461 | 0.2598 | 0.0029 | 8.524695 | 4.87948 | |

3.2 Morphological Analysis

SEM images of pure and Al-doped CdO thin films are shown in Fig. 2. A careful observation of pure CdO surface shows grains like mounts without well-defined boundaries. It can be seen that grains clump together and hence do not display homogeneous distribution for pure CdO samples (Jie *et al.* 2013) (Aswani *et al.* 2014). Average grain size could not be calculated due to clumping (Lee *et al.* 2014) (Colak *et al.* 2013). The particle size is in few nanometer ranges, and it exhibits needle-like structure (Jie *et al.* 2013) (Aswani *et al.* 2014) for Al doped CdO nanopowder. It is observed

that the doping of Al stimulates an obvious change in grain size. Furthermore, the influence of incorporation of Al on the surface morphology of the samples can be clearly seen (Ashok V. Borhade *et al.* 2012; Gupta *et al.* 2008).

3.3 Photo Catalytic Degradation of Azo Dyes of Pure and Al Doped CdO Thin Films

Fig. 3(a) shows the absorbance spectrum of methylene blue (MB) dye degradation using pure Cadmium Oxide thin films under the irradiation of UV light. From the fig., it is clear that the absorbance of MB

is more or less equal to 670nm. When the CdO thin films are dipped for about 4 cm in the freshly prepared MB solution and kept under irradiation of UV light, it is monitored that the absorbance is considerably decreased. The irradiation time is varied from 1 hour to 5 hours. The absorbance value starts decreasing from the first hour of irradiation, and at the fifth hour, the absorbance is found to be reduced significantly. At the first hour of light irradiation, decolorizing efficiency for MB dye solution was achieved to about 11%. This value nearly reached 18% after 5h illumination. This result proves that the synthesized photo catalyst performs remarkably in removing the mentioned azo dyes under visible light illumination in a short time.

In heterogeneous photo catalysis of azoic dyes, the electron-hole pairs will be primarily created by the irradiation of a semiconductor with a photon of energy equal to or better than its bandgap width (Cheng *et al.* 2013). The electrons and holes may drift to the semiconductors on the catalyst surface, where they participate in redox reactions with the adsorbed azoic dyes (Ullah *et al.* 2014). The oxidizing radical could hit the azo dye molecule and disintegrate it into CO₂ and H₂O molecules which are non-hazardous (Soltani and Entezari, 2013; Ullah *et al.* 2014). It has been

recommended that the formation of free radicals acts as a major oxidizing type (Comparelli *et al.* 2005). In the absence of catalyst, decolorization of MB and MO was not observed even after 24 hours, signifying that there was no direct oxidation path. On the other hand, decolorization of MB and MO happened only when CdO was brought into the solution mixtures indicating the essentiality of the films for promoting the decolorization, which perhaps takes place through the free radicals pathway.

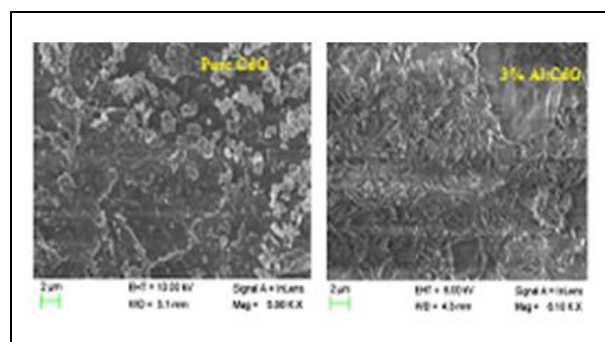


Fig. 2: SEM images of pure and Al doped CdO thin films

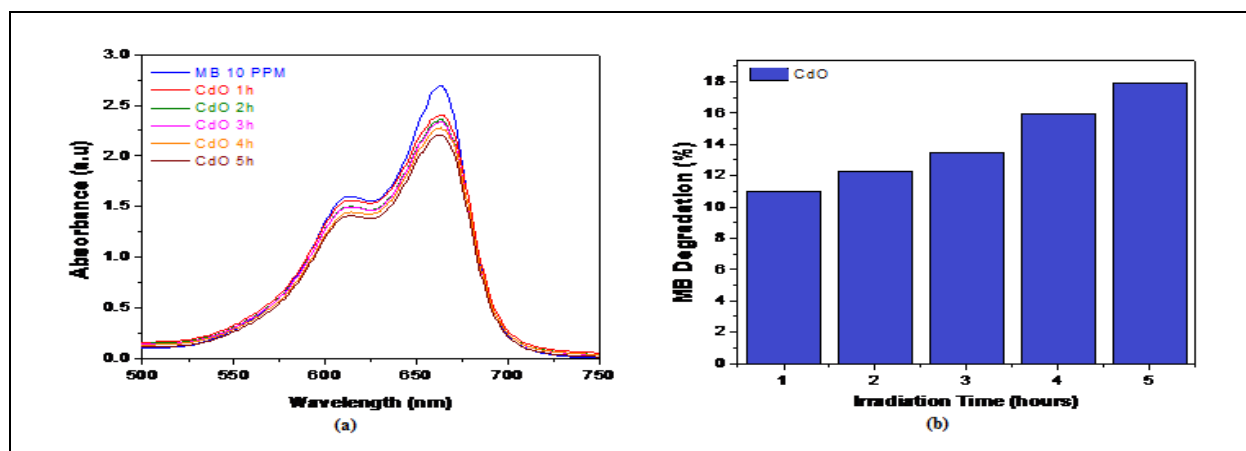


Fig. 3: Absorbance spectrum of MB dye degradation of (a) pure CdO thin films (b) Bar chart of MB degradation by pure CdO

The fig. 4(a) and (b) demonstrate the absorbance of MB by the 3wt% Al doped CdO thin films. To demonstrate the degradation process, the range was recorded at various time intervals (Anour Hajjaji *et al.* 2014). After an illumination time of 1hour, the dye solution MB was destructed by 3 wt% Al doped CdO thin films by about 6%. The photo catalytic process was prolonged for a few more hours, and the maximum degradation of the dye reached 18% after 5hours. The MB reacts with the electrons generated on the CdO particles under UV irradiation.

Fig. 5 (a) explains the absorbance spectrum of Methyl Orange (MO) by pure CdO thin films. The absorbance of MO is at a wavelength of nearly 465nm in visible light. When MO is treated with pure CdO thin films, there is only a slight variation in the absorbance value. The introduction of the thin films may assist the formation of OH⁻ radical through which the degradation of the dye proceeds. In order to exhibit the degradation process, the spectra were recorded at different time intervals (Anour Hajjaji *et al.* 2014).

In the absence of a photocatalyst, no degradation of azo dyes was observed under visible light irradiation (Azadeh Tadjarodi *et al.* 2014). The obtained result also shows that when the CdO thin films were not introduced, there was no degradation of MB and MO under UV and visible irradiation.

The absorbance of MO by Al doped CdO thin films is explained by the fig. 6 (a, b). There is a vast

decline in the absorbance of MO by 3 wt% Al doped CdO films with 5 hours of irradiation. At the beginning of UV irradiation, one can see that there is only 12.5% of photocatalytic degradation of MO. Later, as time goes, 3 wt% Al doped CdO thin films illustrate a maximum of 30% of MO degradation, which is more than double the initial value.

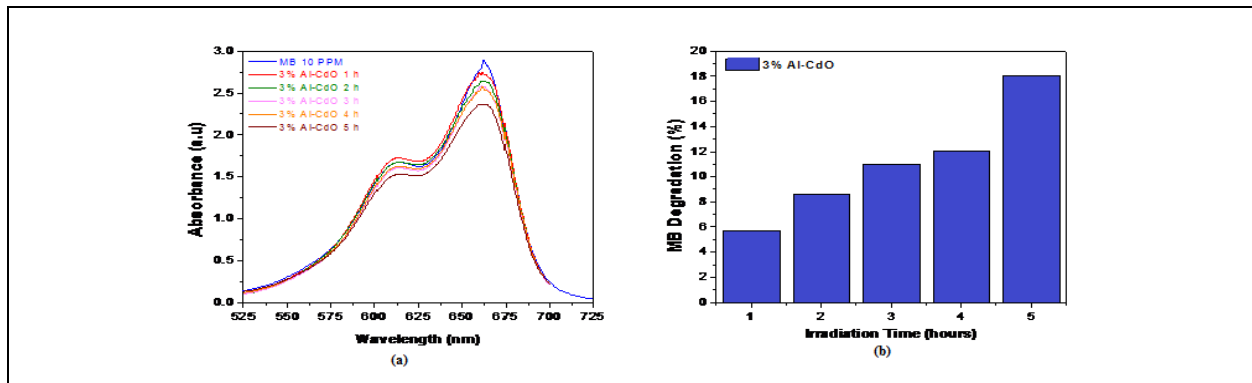


Fig.4: Absorbance of MB dye by (a) 3 wt% Al doped CdO thin films (b) Corresponding Bar chart

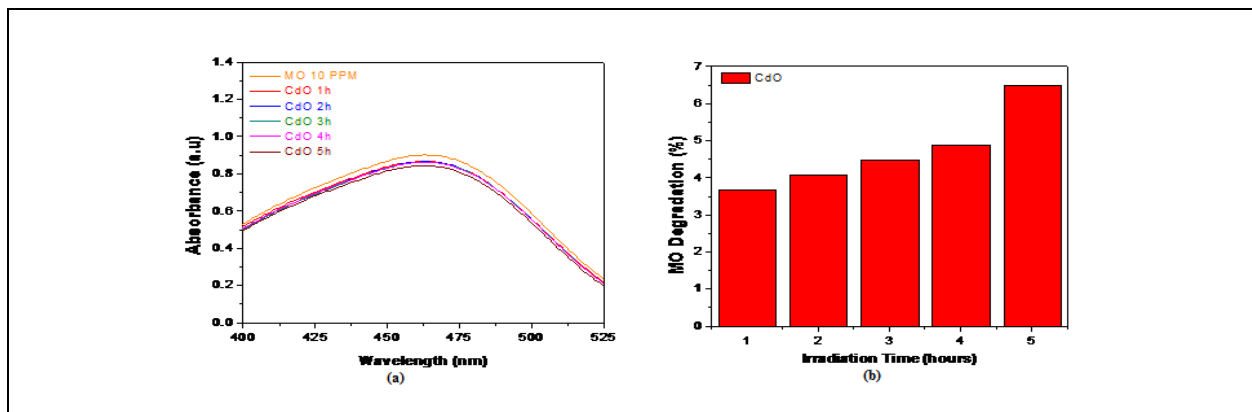


Fig. 5: Absorbance of Methyl orange by (a) pure CdO thin films (b) corresponding bar chart

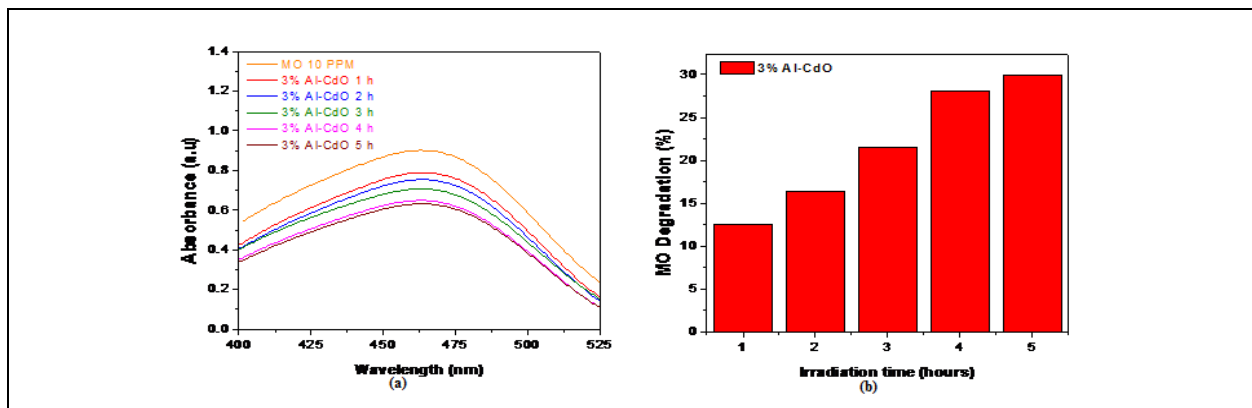


Fig. 6: Absorbance of MO by (a) 3wt% Al doped CdO films (b) Equivalent Bar diagram

This may be because of the enhanced coverage of the semiconductor surface by the metal which diminishes the adsorption sites on the surface, anticipated to be obtainable to the dye. Researchers have demonstrated that an enhanced photo catalytic activity of doped metal oxide is probably due to the acting of metal oxides to trap photo induced electrons, retarding the electron-hole recombination process, and thereby

promoting the photo degradation activity. Similarly, in this work, an enhanced photo catalytic activity of 3 wt% Al doped CdO system may be due to the Al atoms acting to trap photo induced electrons, delaying the process of electron-hole recombination, and so, might have promoted the photo degradation activity. The degradation percentage is calculated for MB and MO individually and is tabulated in Table 2 and Table 3.

Table 2. Degradation % of MB

| MB Degradation- CdO | | | | | |
|---------------------|----------------|----------------|--------------------------------|---|---|
| Time | A ₀ | A _t | A ₀ -A _t | A ₀ -A _t / A ₀ | (A ₀ -A _t /A ₀)*100 |
| 1h | 2.7015 | 2.4039 | 0.2976 | 0.110161 | 11.0161 |
| 2h | 2.7015 | 2.3708 | 0.3307 | 0.122413 | 12.2413 |
| 3h | 2.7015 | 2.3377 | 0.3638 | 0.134666 | 13.4665 |
| 4h | 2.7015 | 2.2716 | 0.4299 | 0.159134 | 15.9134 |
| 5h | 2.7015 | 2.2165 | 0.485 | 0.17953 | 17.9530 |

| MB Degradation 3% Al-CdO | | | | | |
|--------------------------|----------------|----------------|--------------------------------|---|---|
| Time | A ₀ | A _t | A ₀ -A _t | A ₀ -A _t / A ₀ | (A ₀ -A _t /A ₀)*100 |
| 1h | 2.886 | 2.7212 | 0.1648 | 0.057103 | 5.7103 |
| 2h | 2.886 | 2.6382 | 0.2478 | 0.085863 | 8.5863 |
| 3h | 2.886 | 2.5686 | 0.3174 | 0.109979 | 10.9976 |
| 4h | 2.886 | 2.5376 | 0.3484 | 0.120721 | 12.0720 |
| 5h | 2.886 | 2.3665 | 0.5195 | 0.180007 | 18.0007 |

Table 3. Degradation % of MO

| MO Degradation CdO | | | | | |
|--------------------|----------------|----------------|--------------------------------|---|---|
| Time | A ₀ | A _t | A ₀ -A _t | A ₀ -A _t / A ₀ | (A ₀ -A _t /A ₀)*100 |
| 1h | 0.9039 | 0.8708 | 0.0331 | 0.036619 | 3.6619 |
| 2h | 0.9039 | 0.8671 | 0.0368 | 0.040712 | 4.0712 |
| 3h | 0.9039 | 0.8634 | 0.0405 | 0.044806 | 4.4805 |
| 4h | 0.9039 | 0.8598 | 0.0441 | 0.048789 | 4.8788 |
| 5h | 0.9039 | 0.8451 | 0.0588 | 0.065051 | 6.5051 |

| MO Degradation 3% Al-CdO | | | | | |
|--------------------------|----------------|----------------|--------------------------------|---|---|
| Time | A ₀ | A _t | A ₀ -A _t | A ₀ -A _t / A ₀ | (A ₀ -A _t /A ₀)*100 |
| 1h | 0.902 | 0.7896 | 0.1124 | 0.124612 | 12.4611 |
| 2h | 0.902 | 0.7542 | 0.1478 | 0.163858 | 16.3858 |
| 3h | 0.902 | 0.7084 | 0.1936 | 0.214634 | 21.4634 |
| 4h | 0.902 | 0.6493 | 0.2527 | 0.280155 | 28.0155 |
| 5h | 0.902 | 0.6315 | 0.2705 | 0.299889 | 29.9889 |

Once the aqueous semiconductor (CdO) solutions are irradiated in light energy greater than the bandgap energy of the semiconductors, conduction band electrons, and valence band holes are produced (Lee *et al.* 2014; Jiang *et al.* 2013). As the charge separation is sustained, the electrons and holes may drift to the semiconductor surface, where it takes part in the redox reaction with azo dyes (Hamadani *et al.* 2013; Harraz *et al.* 2014; Zhang *et al.* 2013). The electrons generated by light react with the adsorbed dye molecules (O₂⁻) on the semiconductor site and lessen it to superoxide radical anion (O₂⁻) while the photogenerated holes oxidize the H₂O or OH⁻ ions adsorbed at the semiconductor surface to OH⁻ radicals (Jie *et al.* 2013; Shahmoradi *et al.* 2013; Priyanka and Srivastava, 2013). These radicals generated with other high oxidant species work as strong oxidizing agents which could easily hit the adsorbed azo dye molecules or those located close to the surface of the semiconductor, thus resulting in the degradation of azoic dyes (Nurhidayatullaili *et al.* 2014). Thus in the present work also, the degradation of azoic dyes might have been caused by the redox reaction on the semiconductor surface.

4. CONCLUSION

The obtained results demonstrated that the pure and Al doped CdO thin films could degrade azoic dyes (methylene blue and methyl orange) with optimum conditions. It was found that 3 wt% Al doped CdO bleaches methylene blue much better with 19% degradation than the pure CdO thin films upon its exposure to the UV light. Among the two different azoic dyes, methyl orange reacts better and degrading to the maximum of 30%.

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